

# On the isotropic-biaxial phase transition in nematic liquid crystals

G. GAETA

*Dipartimento di Matematica, Università degli Studi di Milano, via Saldini 50, I-20133 Milano (Italy)*

PACS 64.70.M- – Transitions in liquid crystals  
PACS 05.70.Fh – Phase transitions: general studies  
PACS 05.45.-a – Nonlinear dynamics

**Abstract** – We apply a recently developed technique to determine adapted coordinates for the sixth degree Landau-deGennes potential, in which the potential is specially simple, to analyze the possibility of a direct transition between the fully symmetric state and a biaxial phase in nematic liquid crystals. Our results confirm, with simpler computations, results by Allender and Longa.

**Introduction.** – Biaxial phases in nematic liquid crystals [1,2] receive a continuing attention [3]. They have been approached theoretically in many different ways (see e.g. [4–18]) and sought for experimentally [19,20]<sup>1</sup>, but many open questions still exist [3].<sup>2</sup>

One of the widely debated questions concern the possibility of a *direct* transition from the fully symmetric state to a stable biaxial phase, without an intermediate uniaxial phase (generically, the biaxial phase appears in between the prolate and the oblate uniaxial ones [23,24]). Even the simplest theoretical analysis, based on the sixth degree Landau-deGennes (LdG) potential [25,26] – in the context of Landau theory of phase transitions [27,28] – presents many difficulties and intricacies [23,24].

In this Letter, we want to apply a recently proposed method [29–31] for dealing with Landau theory along the lines of (Poincaré-like) canonical perturbation theory [32–35], and in particular its modifications (along the lines of “further normalization” [36–38] in the dynamical systems parlance) to deal with problems involving a phase transition [31].

The difficulty of the concrete problem at hand lies in that even in this simple approach one has to analyze a sixth degree potential depending on the leading parameter  $\lambda$  and five additional ones (two of these could be eliminated by suitably setting the scale for energy and  $Q$ ; we won’t do

that). That is, one is faced with a six-parameters family of sixth degree Landau polynomials.

Our approach consists in separating the problem in two simpler steps. The first and key step is the search for a “normal form” for this family: that is, a smaller family of (sixth degree) Landau polynomials which, upon invertible maps, is in correspondence with the full six-parameter family. Once this smaller family – concretely, a family depending on the leading plus two additional parameters – of simpler Landau polynomials, referred to as the “simplified LdG potential”, is obtained the second step will consist in analyzing it and its critical points with classical tools.

The main idea to implement the first and key step is borrowed from Poincaré normal forms theory<sup>3</sup> for Dynamical Systems [32–34], and consists in using covariant near-identity changes of coordinates [29–31]. This systematizes, using ideas by L. Michel [41,42] and other Authors [43–45], an approach to simplification of Landau potentials which appears to have been pioneered by Gufan [46].

However, as we want to operate in a full neighborhood of the transition point, we should pay attention these changes of coordinates are well defined in all of such a region. An abstract discussion of this point would require to introduce “further normalization” of Poincaré normal forms [36–38]; however here we are concerned with a specific physical application, and all of our computations will be completely explicit; it will thus suffice to check the considered transformations are not singular in the relevant region, and this will simply mean that no division by a factor  $\lambda$  should ever appear, where  $\lambda$  is the parameter related to the quadratic part of the LdG potential, hence controlling the local sta-

<sup>1</sup>This presented substantial difficulties: the first experimental observation [21] came ten years after their theoretical prediction [1,2].

<sup>2</sup>A large body of research has been devoted to biaxial phases for liquid crystals made of molecules which are biaxial themselves, or even have a more complex shape (e.g. V-shaped, or tetrapodes [22]). The biaxial phases considered here could also be constituted by uniaxial molecules, as the order tensor  $Q$  (see below) represents the quadrupolar moment of the molecular uniaxial distribution function.

<sup>3</sup>Application of the Poincaré theory also proved very effective in computing the spectra of simple molecules [39,40].

bility of the isotropic phase, scaled so that the critical value for the local change of stability is  $\lambda = 0$ .

**Landau theory for nematic liquid crystals.** –

Nematic liquid crystals are described by a tensorial order parameter  $Q$  [25, 26]; more precisely, this is a real three-dimensional symmetric traceless matrix, hence parametrized by five real numbers and which can be put in correspondence with a five-dimensional vector  $V = (z_1, \dots, z_5) \in \mathbf{R}^5$ ,

$$Q = \begin{pmatrix} z_1 & z_2 & z_3 \\ z_2 & z_4 & z_5 \\ z_3 & z_5 & -(z_1 + z_4) \end{pmatrix}. \quad (1)$$

The theory is covariant under the adjoint action of  $SO(3)$  on three-dimensional symmetric traceless matrices acting on  $Q$ ; this is also described in terms of the five-dimensional  $SO(3)$  representation acting on  $V$ .

It is well known that this admits two algebraically independent polynomial invariants, which hence also characterize orbits. A convenient choice for these is just

$$T_2 = (1/2) \text{Tr}(Q^2), \quad T_3 = (1/3) \text{Tr}(Q^3). \quad (2)$$

In terms of the components  $z_i$ , these read

$$\begin{aligned} T_2 &= z_1^2 + z_2^2 + z_3^2 + z_4^2 + z_5^2 + z_1 z_4; \\ T_3 &= z_1(z_2^2 - z_4^2 - z_5^2) - z_4(z_1^2 - z_2^2 + z_3^2) + 2z_2 z_3 z_5. \end{aligned} \quad (3)$$

Here  $T_2$  is related to  $q = |Q| = \sqrt{(1/2)\text{Tr}(Q^T Q)}$ , the amplitude of the order parameter  $Q$ , while  $T_3$  is related to both  $q$  and the measure of biaxiality  $\omega$ ; more precisely, we have

$$T_2 = q^2, \quad T_3 = \frac{(1 - \omega)}{\sqrt{6}} q^3. \quad (4)$$

The inverse relations for (4) are of course

$$q = \sqrt{T_2}, \quad \omega = 1 - \sqrt{6 T_3^2 / T_2^3}; \quad (5)$$

we take (the second of) these as the definition of  $\omega$ .

We easily obtain from (3) that

$$\Delta := T_2^3 - 6 T_3^2 \geq 0, \quad (6)$$

which also entails

$$0 \leq \omega \leq 1. \quad (7)$$

Maximally biaxial states  $\omega = 1$  correspond to  $T_3 = 0$ , while uniaxial states  $\omega = 0$  correspond to  $\Delta = 0$ , i.e. to the boundary of the allowed region in the  $(T_2, T_3)$  plane.

When describing nematic liquid crystals in terms of Landau theory [27, 28] one uses the Landau-deGennes (LdG in the following) potential [25]; on general grounds this is the most general invariant (under the adjoint  $SO(3)$  action) sixth order potential, and is therefore written as

$$\begin{aligned} \Phi &= c_1 T_2 + c_2 T_3 + c_3 T_2^2 + c_4 T_2 T_3 \\ &\quad + c_5 T_2^3 + c_6 T_3^2. \end{aligned} \quad (8)$$

Here the  $c_i$  are real parameters, generally depending on the physical parameters (temperature, pressure, etc); we require (for stability)  $c_5 > 0$ ,  $c_5 + 6c_6 > 0$ . The state of the system is described by minima<sup>4</sup> of  $\Phi$ . Obviously for  $c_1 > 0$  the fully symmetric state  $q = 0$  is locally stable, while this becomes locally unstable for  $c_1 < 0$ .

We will thus write  $c_1 = -\lambda$ , and consider  $\lambda$  as the leading parameter in the main transition, taking place for  $\lambda = 0$  as  $\lambda$  is varied. We will assume that the other parameters  $c_i$  are not varied; or at least that their variation is not relevant in the considered region and can be disregarded. Note this requires they are not zero at the transition, i.e. we are not in a multi-critical case.

For  $\lambda > 0$  the isotropic state is locally unstable; the full rotational symmetry is spontaneously broken, and the liquid crystals can in particular show uniaxial ( $\omega = 0$ ) or biaxial ( $\omega \neq 0$ ) states. These states can also be present for  $\lambda < 0$  and a locally stable isotropic state, due to the appearance of lower energy configurations. Note that the transition can also be (and necessarily is for  $\lambda < 0$ ) first order, i.e. the symmetry-breaking states can appear with non-zero amplitude.

A long standing question [15, 23, 24] is if there can be stable branches of biaxial solutions branching off *directly* from the fully symmetric state  $q = 0$  at  $\lambda = 0$ . This matter has been studied by several authors, but the question is still open. An answer in the positive was provided by Allender and Longa [24] in the frame of LdG theory, under rather restrictive conditions on the parameters.

**Change of variables; simplified LdG potential.** –

We want to simplify the LdG potential (8) by using a *near-identity covariant change of coordinates*. Here near-identity means this will be of the form

$$z_i = x_i + h_i(x), \quad (9)$$

with  $h_i$  a nonlinear (polynomial) function of the  $x$ ; covariant means that we should preserve the symmetry properties of the theory, and choose  $\mathbf{h}$  to transform in the same way as  $V$  under the  $G = SO(3)$  action. (Such a change of coordinates amounts to a nonlinear reparametrization of the tensor  $Q$ .)

Covariant vector polynomials (for short, *covariants*) under this  $G$  action are well known; they are generated by two basic ones, i.e. a linear one,

$$\mathbf{F}_1 = \mathbf{x} = (x_1, x_2, x_3, x_4, x_5)^T;$$

and a quadratic one,

$$\mathbf{F}_2 = \begin{pmatrix} (x_1^2 + x_2^2 + x_3^2) - 2(x_1 x_4 + x_4^2 + x_5^2) \\ 3(x_1 x_2 + x_2 x_4 + x_3 x_5) \\ 3(x_2 x_5 - x_3 x_4) \\ (x_2^2 + x_4^2 + x_5^2) - 2(x_1^2 + x_3^2 + x_1 x_4) \\ 3(x_2 x_3 - x_1 x_5) \end{pmatrix}. \quad (10)$$

<sup>4</sup>One can check there are four nontrivial branches – i.e.  $q \neq 0$  – of critical points for  $\Phi$ ; some of these might be un-physical, i.e. with  $q < 0$ , depending also on the parameter values.

The product of a (scalar) invariant and a (vector) covariant is of course a covariant; thus the list of low order covariant vectors is as follows:

$$\mathbf{F}_1 = \mathbf{x}, \mathbf{F}_2, \mathbf{F}_3 = T_2 \mathbf{x}, \mathbf{F}_4^{(1)} = T_3 \mathbf{x}, \mathbf{F}_4^{(2)} = T_2 \mathbf{F}_2.$$

We will hence consider a change of variables of the form (9), with (it suffices to consider terms of degree not higher than four)

$$\mathbf{h} = k_1 \mathbf{F}_2 + k_2 \mathbf{F}_3 + k_3 \mathbf{F}_4^{(1)} + k_4 \mathbf{F}_4^{(2)}; \quad (11)$$

here the  $k_i$  are arbitrary real constants, to be chosen appropriately in a moment. It can be checked that with this, the LdG potential  $\Psi$  is changed into a potential of the same form, i.e.

$$\begin{aligned} \Phi &= c_1 T_2 + \gamma_2 T_3 + \gamma_3 T_2^2 + \gamma_4 T_2 T_3 \\ &\quad + \gamma_5 T_2^3 + \gamma_6 T_3^2 + O(x^7); \end{aligned} \quad (12)$$

explicit expression for the coefficients  $\gamma_i$  can be easily obtained with straightforward algebra. They become slightly simpler by assuming, as we do in the following,  $k_1 = 0$ ; in this case they are given explicitly by

$$\begin{aligned} \gamma_2 &= c_2, \\ \gamma_3 &= c_3 + 2c_1 k_2, \\ \gamma_4 &= c_4 + 3c_2 k_2 + 2c_1 k_3 + 9c_1 k_4, \\ \gamma_5 &= c_5 + c_1 k_2^2 + 4c_3 k_2 + 2c_2 k_4, \\ \gamma_6 &= c_6 + 3c_2 k_3. \end{aligned}$$

We would then like to choose the  $k_i$  so to have as simple as possible a potential  $\Phi$ . By this we mean one would like to eliminate some of the terms (i.e. get some of the  $\gamma_i$  to vanish). Note however that in order to guarantee thermodynamic stability of the theory,  $\Phi$  should be convex for large  $|\mathbf{x}|$ . A simple way to guarantee this is by having  $\eta |\mathbf{x}|^{2k}$  (in this case with  $k = 3$ ), where  $\eta$  is some positive constant, as the highest order term.

We will work under the *non-degeneracy assumption*

$$c_2 \neq 0; \quad (13)$$

this means that at the phase transition the next-to-leading order term is not vanishing. In some of our considerations we will also assume, for the sake of simplicity in the discussion, that  $c_3 \neq 0$ .

It is easily checked that requiring

$$\gamma_4 = 0, \quad \gamma_5 = 1, \quad \gamma_6 = 1 \quad (14)$$

admits a solution for  $k_2, k_3, k_4$  which is easily computed by an algebraic manipulation program; full formulas are rather bulky and thus omitted, but disregarding contributions of order  $\lambda$  we get

$$\begin{aligned} k_1 &= 0, \\ k_2 &= -\frac{c_4}{3c_2} + O(\lambda), \\ k_3 &= \frac{1 - c_6}{3c_2}, \\ k_4 &= \frac{3c_2 + 4c_3 c_4 - 3c_2 c_5}{6c_2^2} + O(\lambda). \end{aligned}$$

With this choice we obtain

$$\begin{aligned} \gamma_2 &= c_2, \\ \gamma_3 &= c_3 + [(2c_4)/(3c_2)]\lambda + O(\lambda^2), \\ \gamma_4 &= 0, \\ \gamma_5 &= 1, \\ \gamma_6 &= 1. \end{aligned}$$

The full expression for  $\gamma_3$  is rather involved and not reported here; note that for  $c_3 \neq 0$  the sign of  $\gamma_3$  at small  $\lambda$  is just that of  $c_3$ , while for  $c_3 = 0$  it depends on the signs of  $c_2$  and  $c_4$ .

Hence the LdG potential is reduced to

$$\hat{\Phi} = -\lambda T_2 + \gamma_2 T_3 + \gamma_3 T_2^2 + T_2^3 + T_3^2. \quad (15)$$

In terms of the physical  $(q, \omega)$  variables this reads

$$\hat{\Phi} = -\lambda q^2 + \frac{\gamma_2}{\sqrt{6}}(1 - \omega)q^3 + \gamma_3 q^4 + \left[1 + \frac{1}{6}(1 - \omega)^2\right]q^6.$$

Note that with this choice, and the notation introduced above, we get  $\eta = 1 + [(1 - \omega)^2/6]$ ; in view of (7) this satisfies  $1 \leq \eta \leq 7/6$ .

It is maybe worth remarking that the reduced potential depends essentially on  $c_2$  and  $c_3$ , while dependence on other parameters is rather weak and embodied in  $\gamma_3$ . Recalling that this simplified potential is valid in a neighborhood of the transition point and for small  $|q|$ , the fact that only lower order terms are relevant is certainly not a surprise.<sup>5</sup>

It should be stressed that the nonlinear changes of coordinates considered here produce higher order terms; in our procedure we are only considering terms up to order six, i.e. we are truncating the simplified LdG potential. This amounts to considering a perturbation (small if working near zero) of the original potential. It is in principles possible that the perturbed (i.e. truncated) potential will display a qualitatively different set of critical points than the original one; but if this happens it means that the original LdG potential was *not structurally stable*. This appears not to be the case here.

### Study of the simplified LdG potential (15). –

We should now study the potential (15), and in particular its minima. It is convenient to perform this study in orbit space, i.e. directly with the coordinates  $T_2, T_3$  [41, 42].

Critical points are identified as solutions to

$$\begin{aligned} \frac{\partial \Phi}{\partial T_2} &= -\lambda + 2\gamma_3 T_2 + 3T_2^2 = 0 \\ \frac{\partial \Phi}{\partial T_3} &= \gamma_2 + 2T_3 = 0; \end{aligned} \quad (16)$$

<sup>5</sup>Degenerate (multi-critical) situations, with (13) not holding or with some of the higher coefficients vanishing at the transition point, can be analyzed along the same lines.

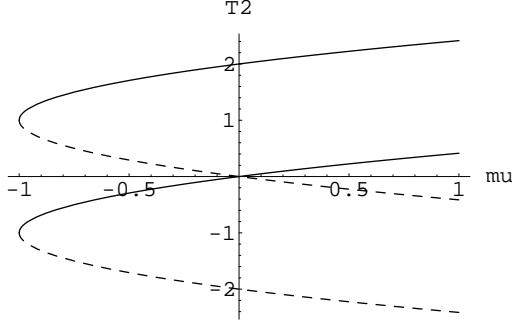


Fig. 1: The value of  $T_2$  as a function of  $\mu$  along the solutions (19), for  $K = 1$ . Solid (dashed) curves refer to  $\alpha = 1$  ( $\alpha = -1$ ). The upper (lower) horizontal parabola is for  $\sigma = -1$  ( $\sigma = +1$ ). Only states with  $T_2 \geq 0$  have physical meaning, due to  $T_2 = q^2$ .

these yield immediately<sup>6</sup>

$$T_2 = \frac{1}{3} \left( -\gamma_3 + \alpha \sqrt{\gamma_3^2(1+\mu)} \right), \quad T_3 = -\gamma_2/2; \quad (17)$$

here and in the following  $\alpha = \pm 1$  and we write

$$\mu = 3\lambda / \gamma_3^2. \quad (18)$$

The solutions (17) exist only for  $\mu \geq -1$ ; this will be understood without further notice from now on. It should also be stressed that  $T_2 = q^2$  requires  $T_2 \geq 0$  for the solutions to be physically relevant; see Fig.1.

Our discussion will depend on the signs of  $\alpha$  and of  $\gamma_3$ ; it is thus convenient to write  $\gamma_3 = \sigma g$  with  $g = |\gamma_3| \geq 0$  and  $\sigma = \pm 1$ . It will also be convenient to write  $g = 3K^2$ , i.e.  $\gamma_3 = 3\sigma K^2$  (say with  $K > 0$ ).

In this way the solutions (17) read simply

$$T_2 = K^2 \left( -\sigma + \alpha \sqrt{1+\mu} \right), \quad T_3 = -\gamma_2/2. \quad (19)$$

We thus have again – as for the original LdG potential – four nontrivial branches, indexed by the signs of  $\alpha$  and  $\sigma$ ; some of these might be un-physical ( $q < 0$ ), also depending on the parameters values; see Fig.1 and the discussion below.

Note that  $dT_2/d\mu = \alpha[K^2/(2\sqrt{1+\mu})]$ , i.e.  $T_2$  is strictly increasing (decreasing) with  $\mu$  for  $\alpha = 1$  (for  $\alpha = -1$ ).

The local stability of the solutions (17), (19) can be simply analyzed by considering the Hessian  $H$  for the potential (15) at these solutions. With trivial computations,  $H$  and its eigenvalues  $\zeta_i$  are given by

$$H = \begin{pmatrix} 2\gamma_3 + 6T_2 & 0 \\ 0 & 2 \end{pmatrix}; \quad \zeta_1 = 2, \quad \zeta_2 = 2(\gamma_3 + 3T_2); \quad (20)$$

thus along the solutions (17) we have

$$\zeta_2 = \alpha \sqrt{\gamma_3^2(1+\mu)} = 3\alpha K^2 \sqrt{1+\mu}. \quad (21)$$

<sup>6</sup>Note we are missing the trivial solution  $q = 0$ ; this is due to the change of variable (4) or (5) being singular at  $q = 0$ .

In conclusion, the solutions with  $\alpha = 1$  ( $\alpha = -1$ ) are always locally stable (unstable).

We thus have four different branches of nontrivial solutions, indexed by the signs of  $\alpha$  and  $\sigma$ ; these will be denoted as  $S_{(\pm\pm)}$ . As mentioned above,  $T_2 = q^2$  should be positive to have physical meaning; it is immediately seen that for  $\mu > 0$  only  $\alpha = +1$  is allowed. Similarly, for  $\mu < 0$ , only  $\sigma = -1$  is allowed. Thus  $S_{(+-)}$  is allowed for all  $\mu > -1$ , while  $S_{(++)}$  only for  $\mu \geq 0$  and  $S_{(--)}$  only for  $\mu \leq 0$ ; the latter one is locally unstable and thus not of physical interest.

Let us now consider the  $(q, \omega)$  variables. It follows immediately from  $q = \sqrt{T_2}$  that

$$q = K \sqrt{-\sigma + \alpha \sqrt{1+\mu}}; \quad (22)$$

this produces, once the signs of  $\alpha$  and  $\sigma$  are chosen, a “universal” behavior for

$$\chi := q/K = \sqrt{-\sigma + \alpha \sqrt{1+\mu}}. \quad (23)$$

In the limit  $\mu \rightarrow 0$  we get  $q \rightarrow K\sqrt{\alpha - \sigma}$ ; thus we have solutions branching off the fully isotropic one for  $\alpha = \sigma$ . We will also have solutions which are *not* branching off the fully isotropic one, corresponding to  $\sigma = -\alpha$  as in  $S_{(+-)}$ .

As for  $\omega$ , it follows from (5) that

$$\omega = 1 - \frac{|\gamma_2|}{\alpha K^3} \sqrt{\frac{3}{2}} \left( \frac{1}{\sqrt{1+\mu} - \sigma} \right)^{3/2}. \quad (24)$$

For given  $\alpha$  and  $\sigma$  we have a “universal” behavior for

$$\theta := \sqrt{\frac{2}{3}} \frac{K^3}{|\gamma_2|} (1 - \omega) = \frac{1}{\alpha} \left( \frac{1}{\sqrt{1+\mu} - \sigma} \right)^{3/2}. \quad (25)$$

It is immediately seen that if  $\sigma = 1$  then  $\omega$  is singular for  $\mu \rightarrow 0$ , so that (7) is surely not satisfied at the branching point  $\mu = 0$  (it might be satisfied for larger values of  $|\mu|$ ). For  $\sigma = -1$  the requirement (7) can be satisfied for  $\mu \rightarrow 0$  provided  $\alpha = 1$  and depending on the values of  $\gamma_2$  and of  $K$ , i.e. for  $4K^3 \geq |\gamma_2|\sqrt{3}$ . Recalling  $K = \sqrt{|\gamma_3|/3}$  this reads

$$4|\gamma_3|^{3/2} \geq 9|\gamma_2|. \quad (26)$$

The situation is summarized in the following table; here “loc stab” stands for locally stable, and  $(q_0, \omega_0)$  is the limit of  $(q, \omega)$  for  $\mu \rightarrow 0$ .

	loc stab	$q_0 = 0$	$0 \leq \omega_0 \leq 1$
$S_{(++)}$	yes	yes	no
$S_{(+-)}$	yes	no	see (26)
$S_{(--)}$	no	yes	no

It is clear from this table that no continuous (second order) transition from the isotropic to a new stable state satisfying the  $\omega$ -condition (7), hence (26), is allowed at  $\lambda = 0$ . On the other hand, other types of transitions could and will be possible.

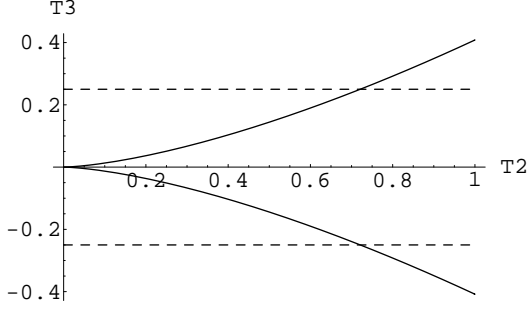


Fig. 2: Solid lines represent the boundary of the region satisfying (6), i.e. (7); on the boundary of this region,  $\omega = 0$  (on the line  $T_3 = 0$ ,  $\omega = 1$ ). The lines  $T_3 = \pm\gamma_2/2$  are in the region for  $T_2 \geq L$ . Here  $\gamma_2 = 1/2$ , which by (29) yields  $L \simeq 0.72$ .

We stress that the above table considers the  $\omega$ -condition (7) only at the branching point  $\mu = 0$ . It is well possible that a solution does not fulfill it at  $\mu = 0$  but complies with it at larger values of  $|\mu|$ .

For general values of  $\mu$ , the condition (7) is better studied via the equivalent formulation (6). On solutions this reads

$$\Delta = K^6 \left( \alpha \sqrt{1+\mu} - \sigma \right)^3 - (3/2) \gamma_2^2; \quad (27)$$

thus (6) requires

$$\left( \alpha \sqrt{1+\mu} - \sigma \right)^3 \geq \frac{3}{2} \frac{\gamma_2^2}{K^6} = \frac{81}{2} \frac{\gamma_2^2}{|\gamma_3|^3}. \quad (28)$$

Looking back at (6), it is clear that the  $\omega$ -condition is satisfied for  $|T_3| \leq \sqrt{T_2^3/6}$  (with  $\omega = 0$  on the boundary of this region); on the other hand, we know that  $T_2$  is monotone with  $\mu$ , and that on solutions  $T_3 = -\gamma_2/2$ . Thus (see fig.2) the  $\omega$ -condition is satisfied along the solution for

$$|T_2| \geq L := [(3/2) \gamma_2^2]^{1/3}. \quad (29)$$

The condition (29) will provide different conditions on the values of  $\mu$  for different solutions, i.e. for different signs of  $\alpha$  and  $\sigma$ . At a given  $\mu$ , the stable physical state will be the one with the lowest energy among those satisfying the  $\omega$ -condition.

In view of (29) the limit value  $\mu_{\pm}^*$  (which will be a lower limit for  $\alpha = 1$ ) of  $\mu$  for the  $\omega$ -condition to be satisfied on the solution  $S_{(+\pm)}$  is<sup>7</sup>

$$\mu_{\sigma}^* = \frac{L(L + 2\sigma K^2)}{K^4}. \quad (30)$$

Note that  $\mu_+^* > 0$ , and it is always  $\mu_-^* < \mu_+^*$ .

<sup>7</sup>In case it results  $\mu_+^* < 0$ , this should be meant as  $\mu_+^* = 0$ , as  $S_{(++)}$  is only meaningful for  $\mu \geq 0$ ; similarly, if  $\mu_-^* < -1$ , this should be meant as  $\mu_-^* = -1$ .

We should now evaluate the energy of states corresponding to the solutions  $S_{(\pm\pm)}$ . On these the simplified potential (15) is trivial for  $K = 0$ , and for  $K \neq 0$  it reads

$$\Phi_{\sigma} = K^6 \left[ (2 + 3\mu) \sigma - 2 \sqrt{(1+\mu)^3} - \frac{\gamma_2^2}{4K^6} \right]. \quad (31)$$

Note that  $\Phi_+$  is defined for  $\mu \geq 0$ , while  $\Phi_-$  for  $\mu \geq -1$ ; when both of them are defined ( $\mu \geq 0$ ), then  $\Phi_+ - \Phi_- = 2K^6(2 + 3\mu) > 0$ . Thus (recalling also  $\mu_-^* < \mu_+^*$ ) the competition for the lower energy is always between the isotropic state  $S_0$ , with energy  $\Phi_0 = 0$ , and the state identified by  $S_-$  with energy

$$\Phi_- = -K^6 \left[ \gamma_2^2/(4K^6) + \left( 2 + 3\mu + 2(1+\mu)^{3/2} \right) \right]; \quad (32)$$

for  $\mu > 0$  it is always  $\Phi_- < \Phi_0 = 0$ , but it is clear this will also hold for some range of negative  $\mu$ , i.e. for  $\mu > \mu_0$  with  $\mu_0 < 0$ .

We conclude that the state described by the solution  $S_{(+\pm)}$  exists for  $\mu \geq \mu_-^*$ , and is stable for  $\mu > \max(\mu_-^*, \mu_0)$ . As seen above, both  $\mu_-^*$  and  $\mu_0$  are strictly negative; thus there is *always* a range of negative  $\mu$  (hence negative  $\lambda$ ) for which the symmetry breaking solution is stable.

If  $\mu_-^* > \mu_0$ , the symmetry breaking solution will appear with  $\omega = 0$  and will then grow into a solution with  $\omega \neq 0$ ; but if instead  $\mu_-^* < \mu_0$ , the symmetry breaking solution will appear with  $\omega \neq 0$ . That is, in this case we have a direct transition to a biaxial phase.

We would of course like to have some information about the range of parameters allowing for such a situation. Noting that

$$\frac{d\Phi_-}{d\mu} = -K^6 \left( 1 + \sqrt{1+\mu} \right) < 0, \quad (33)$$

it suffices to investigate if  $\Phi_* := \Phi_-(\mu_-^*)$  is positive (in which case  $\mu_0 > \mu_-^*$ ) or negative (in which case  $\mu_0 < \mu_-^*$ ).

Writing  $\eta := |(L - K^2)/K^2|$ , it results

$$\Phi_* = -\frac{L^3}{6} - 2(1+\eta)K^6 - L^2(3+2\eta)K^2 + 2L(3+2\eta)K^4. \quad (34)$$

A numerical investigation (see Fig.3) shows that there is a range of parameters for which this is positive.

**Conclusions.** — Considering Poincaré-like changes of coordinates holding in a full neighborhood of  $\lambda = 0$ , the LdG potential of degree six, depending on six parameters, can be led to a form involving only three parameters.

The dependence on a smaller number of parameters allows to perform easily a perturbation analysis near  $\lambda = 0$ , at least under the non-degeneracy assumption (13); this amounts to requiring that the next-to-leading order term does not vanish together with the leading order term and is thus a natural – and generically satisfied – condition.

We have showed that under this hypothesis – and within the sixth degree Landau-deGennes theory – when passing



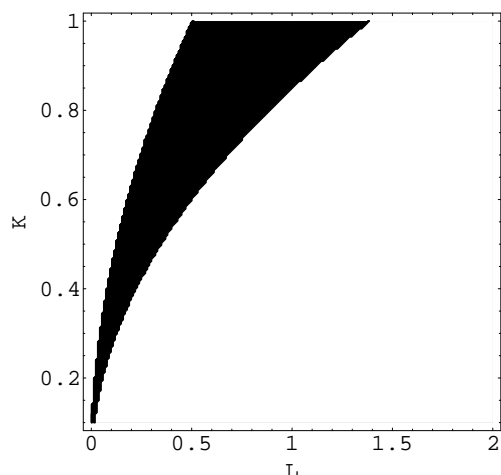


Fig. 3: The black region in the parameter space is the one where  $\Phi_*$ , defined in (34), is positive.

to the simplified LdG potential there is no stable biaxial solution branching off directly from the fully symmetric state via a second order transition. On the other hand, depending on the relation between the two critical parameters  $\mu_-^*$  and  $\mu_0$  defined above, there can be a direct first order transition from the fully isotropic to a biaxial phase.

This result should be compared with the one reported by Allender and Longa [24]; they found that a stable biaxial phase is present, and a direct transition from the fully isotropic state to this phase is possible, for certain values of the parameters. Thus our approach obtains the same qualitative results as the standard one in this case.

\*\*\*

This work originated in the Program “Mathematics of Liquid Crystals” at the Newton Institute. My research is partially supported by MIUR-PRIN program under project 2010-JJ4KPA. I would like to thank the referees for interesting and very useful constructive remarks.

## REFERENCES

- [1] M.J. Freiser, *Phys. Rev. Lett.* **24** (1970), 1041-1043
- [2] M.J. Freiser, *Mol. Cryst. Liq. Cryst.* **14** (1971), 165-182
- [3] G.R. Luckhurst and T.J. Sluckin (Editors), “Biaxial Nematic Liquid Crystals”, Wiley 2015
- [4] R. Berardi and C. Zannoni, *J. Chem. Phys.* **113** (2000), 5971-5979
- [5] A.M. Sonnet, E.G. Virga and G.E. Durand, *Phys. Rev. E* **67** (2003), 061701
- [6] F. Bisi *et al.*, *Phys. Rev. E* **73** (2006), 051709
- [7] G. De Matteis and E.G. Virga, *Phys. Rev. E* **71** (2005), 061703
- [8] L. Longa *et al.*, *Phys. Rev. E* **71** (2005), 051714

- [9] P. Grzybowski, Ph.D. Thesis, *arXiv:0907.1044*
- [10] P.K. Karahaliou *et al.*, *J. Chem. Phys.* **131** (2009), 124516
- [11] P. Grzybowski and L. Longa, *Phys. Rev. Lett.* **107** (2011), 027802
- [12] S. Dhakal and J.V. Selinger, *Phys. Rev. E* **83** (2011), 020702(R)
- [13] T. To, Ph.D. Thesis, <http://eprints.soton.ac.uk/340040/>
- [14] D. Chillingworth, *Nonlinearity* **28** (2015), 1483-1537
- [15] L. Longa, “Landau theory of nematic phases”; in [3] (pp. 133-151)
- [16] R. Berardi and C. Zannoni, “Computer simulations of biaxial nematics”; in [3], (pp. 153-184)
- [17] I.W. Stewart, “Continuum theory of biaxial nematic liquid crystals”; in [3] (pp. 185-203)
- [18] A.R.D. Close and C. Tronci, *Proc. R. Soc. Lond. A*, **471** (2015), 20150308
- [19] P.D. Brimicombe, “Applications”; in [3] (pp. 215-228)
- [20] G.R. Luckhurst, “Biaxial nematics: order parameters and distribution functions”; in [3] (pp. 25-54)
- [21] L.J. Yu and A. Saupe, *Phys. Rev. Lett.* **45** (1980), 1000-1003
- [22] K. Merkel *et al.*, *Phys. Rev. Lett.* **93** (2004), 237801
- [23] E.F. Gramsbergen, L. Longa and W.H. de Jeu, *Phys. Rep.* **135** (1986), 195-257
- [24] D. Allender and L. Longa, *Phys. Rev. E* **78** (2008), 011704
- [25] P.G. de Gennes and J. Prost, “The Physics of liquid crystals”, Oxford UP 1993
- [26] E. Virga, “Variational theories for liquid crystals”, Chapman & Hall 1995
- [27] L.D. Landau, *Nature* **138** (1936), 840-841; *Zh. Exsp. Teor. Fiz.* **7** (1937), 19-47 & 627-637
- [28] L.D. Landau and E.M. Lifshitz, “Statistical Physics”, Pergamon Press 1958
- [29] G. Gaeta, *Ann. Phys. (NY)* **312** (2004), 511-540
- [30] G. Gaeta, *J. Math. Phys.* **56** (2015), 083504
- [31] G. Gaeta, *J. Math. Phys.* **56** (2015), 083505
- [32] V.I. Arnold, “Geometrical methods in the theory of ordinary differential equations”, Springer 1983
- [33] V.I. Arnold and Yu.S. Ilyashenko, “Dynamical systems I. Ordinary differential equations”, Springer 1988
- [34] C. Elphick *et al.*, *Physica D* **29** (1987), 95-127 & **32** (1988), 488
- [35] G. Cicogna and S. Walcher, *Acta Appl. Math.* **70** (2002), 95-111
- [36] G. Cicogna and G. Gaeta, “Symmetry and perturbation theory in nonlinear dynamics”, Springer 1999
- [37] G. Gaeta, *Ann. I.H.P. Phys. Theo.* **70** (1999), 461-514; *Lett. Math. Phys.* **42** (1997), 103-114 & **57** (2001), 41-60
- [38] G. Gaeta, *Acta Appl. Math.* **70** (2002), 113-131
- [39] M. Joyeux, *J. Chem. Phys.* **109** (1998), 2111-2122
- [40] D. Sugny and M. Joyeux, *J. Chem. Phys.* **112** (2000), 31-39
- [41] L. Michel, *Rev. Mod. Phys.* **52** (1980), 617-651
- [42] L. Michel, J.S. Kim, J. Zak and B. Zhilinskii, *Phys. Rep.* **341** (2001), 1-395
- [43] M. Abud and G. Sartori, *Ann. Phys. (NY)* **150** (1983), 307-372
- [44] P. Chossat and R. Lauterbach, “Methods in equivariant bifurcation theory and dynamical systems”, World Scientific 2000
- [45] P. Chossat, *Acta Appl. Math.* **70** (2002), 71-94
- [46] Yu.M. Gufan, “Structural phase transitions”, Nauka 1982